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Antifouling Effectiveness of Copolymers for Ship Hull Protection

C. A. Dooley

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**Antifouling Effectiveness of
Copolymers for
Ship Hull Protection**

C. A. Dooley

**NAVAL COMMAND, CONTROL AND
OCEAN SURVEILLANCE CENTER
RDT&E DIVISION
San Diego, California 92152-5001**

J. D. FONTANA, CAPT, USN
Commanding Officer

R. T. SHEARER
Executive Director

ADMINISTRATIVE INFORMATION

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Released by
C. Clavell, Jr., Head
Chemistry/Biochemistry
Branch

Under authority of
P. F. Seligman, Head
Environmental Sciences
Division

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SUMMARY

OBJECTIVE

Organotin-copolymer marine antifouling coatings contain tributyltin, which is hydrolyzed from a polymer backbone upon exposure to water. These toxicants affect the larval forms of marine fouling organisms. The objective of this work was to modify the toxicant molecule, tributyltin, to make its use more environmentally acceptable.

RESULTS

Triorganotin toxicants composed of mixed saturated and unsaturated four-carbon chains with double bonds at C-1 and C-3 were prepared. Incorporation of these compounds into random 50:50 copolymers of methacrylic acid and methylmethacrylate resulted in three copolymer compositions with promising physical properties for use as antifouling coatings for ship hulls. These formulations were screened for stability and antifouling in San Diego Bay.

Copolymers of methylmethacrylate and methacrylic acid esterified with dibutyl-3-butenyltin (B-31) and butyldi-3-butenyltin (B-32) show antifouling performance equivalent to copolymer containing tributyltin (B-00) after 6 months in the field. Release rate studies show that a minimum of 25% tin-bearing monomer is necessary for good antifouling properties for all formulations. Degradation of the toxicant species with double bonds, through loss of organic chains, appears to be near simultaneous with its release, through hydrolysis of the ester bond, from the coating. Thus, after prevention of fouling by surface toxicity to target organisms, the released species has a minimal impact on the environment.

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INTRODUCTION

Tributyltin compounds began to replace the standard copper toxicant in marine antifouling coatings in the 1970s, promising a longer service life and savings in fuel and maintenance costs. However, the use of tributyltin compounds as antifoulants for ships' hulls became of increasing concern because of their persistence in the water column and sediments and because of the potential for bioaccumulation. Federal and State restrictions were placed on the use of these highly effective antifouling coatings.

Organotin-copolymer marine antifouling coatings contain tributyltin, which is hydrolyzed from a polymer backbone upon exposure to water. These toxicants affect the larval forms of the marine fouling organisms. Under combined Independent Research/Independent Exploratory Development (IR/IED) funding, the toxicant molecule, tributyltin, was modified to make its use more environmentally acceptable.

One key issue in the use of organotins is the rate of degradation of the toxicant, by loss of one or more of the organic chains from the tin atom, to less or nontoxic species after its release from the coating matrix. It is known from the literature that when ethyl and propyl groups in tetraorganotins are replaced by their unsaturated analogues, vinyl and allyl groups, the resulting compounds show enhanced chemical reactivity (Davies & Smith, 1982; Cochran et al., 1982; Ingham, Rosenberg, & Gilman, 1960). In an attempt to create less stable, and therefore more degradable compounds, we synthesized organotin compounds in which butyl groups were replaced with butenyl groups. Such compounds, used as antifoulants, might be expected to degrade more quickly in the environment while retaining sufficient toxicity to target organisms.

EXPERIMENTAL

CHEMICALS

Dibutyltin dichloride, butyltin trichloride, 1-bromo-1-butene, and 2,2'-azobis-2-methyl-propionitrile were obtained from Pfaltz & Bauer (Waterbury, CT). Resublimed magnesium chips and tributyltin chloride were obtained from Alfa Products (Danvers, MA). Methylmethacrylate, methacrylic acid, tri-n-butyltin chloride, tri-n-butyltin bromide, and 4-bromo-1-butene were obtained from Aldrich Chemical Company (Milwaukee, WI). All were used without further purification. Clean seawater for release rate studies was obtained directly from the seawater flume at the Scripps Institution of Oceanography pier in La Jolla, CA.

INSTRUMENTATION

Compound identifications were obtained with a Hewlett-Packard Model 5890A Gas Chromatograph directly connected to a Hewlett-Packard Model 5970 Mass Selective

Detector (GC/MS). Data collection and reduction were performed with a Hewlett-Packard 9000-300 computer using Model 59970C ChemStation software. Samples were introduced by splitless injection onto a 12.5-m by 0.2-mm ID fused silica capillary column with 0.33- μ m-thick HP-1 coating. Helium carrier gas was used at a head pressure of 40 kPa. The oven was programmed to 230°C at 30°C/min, after an initial 2-minute hold at 50°C. Injector, transfer line and detector were at 250°C. Full spectra were obtained between 50 and 450 atomic mass units. For identification of compounds in seawater at low concentrations, analysis was performed in selected ion mode at mass/charge 311, 313, 315, 317, 319, 341, 343, 345, and 347, which served to differentiate the parent and degradation compounds.

Infrared spectrometry identified the position of the double bond and showed that double bond position was retained after bromination of the compound, that bromine addition across the double bond did not occur, and that the double bond was retained in the polymerized product. The C=C vibration was found at approximately 1600 cm^{-1} and 1640 cm^{-1} for the 1-butenyltin and the 3-butenyltin compounds, respectively (Dooley & Testa, 1989b). Infrared spectra of the neat compounds and polymers were obtained with a BioRad FTS-60 Fourier Transform Infrared Spectrometer.

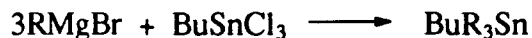
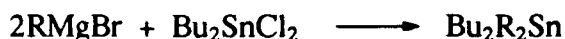
Trace quantities of organotins in seawater samples were analyzed by purge and trap/hydride derivatization, followed by atomic absorption detection. The instrumentation and analytical procedure have been fully described elsewhere (Valkirs et al., 1985; Stallard, Cola, & Dooley, 1989). Briefly, a sample was placed in a modified gas washing bottle and acidified to pH 5.0 to 5.5 with 10% acetic acid. Tin hydride derivatives were formed by the addition of 4% sodium borohydride (NaBH_4) prepared in 1% aqueous sodium hydroxide. The hydride species were subsequently purged from solution and trapped in a glass U-tube packed with 3% OV-1 on 80/100 mesh chromosorb w/hp and immersed in liquid nitrogen during the purging period. The butyltin species were separated and detected sequentially according to their boiling points as they distilled from the trap upon its removal from the liquid nitrogen bath. Detection was accomplished in a quartz burner mounted in a spectrometer using a hydrogen-air flame. Organotin hydrides were detected at 286.3 nm with a Buck Scientific model 200 Atomic Absorption Spectrometer fitted with a tin hollow cathode lamp. The absorbance data were recorded on a Shimadzu CR3A Chromatopac recorder as peak areas.

SYNTHESIS OF COMPOUNDS

Dibutyl-di-1-butenyltin, butyltri-1-butenyltin, tetra-1-butenyltin, dibutyl-di-3-butenyltin, butyltri-3-butenyltin, and tetra-3-butenyltin were prepared via the Grignard reaction (O'Brien, et al., 1971; Vijayaraghavan, 1945; Rosenberg, Gibbons, & Ramsden, 1957; Seyferth & Stone, 1957; Clark & Poller, 1970). The appropriate Grignard reagent was prepared from approximately 10 g of 1-bromo-1-butene or 4-bromo-1-butene in 10 mL anhydrous tetrahydrofuran and an excess of magnesium chips.



where R = the butenyl moiety. The Grignard reagent was decanted from the excess magnesium chips, then cooled to 0°C. A stoichiometric amount of dibutyltin dichloride, butyltin trichloride, or anhydrous tin (IV) tetrachloride in 10 mL of hexane was added dropwise to the stirred solution. The mixture was refluxed for 4 hours.



where Bu = butyl group and R = 1- or 3-butenyl group.

The reaction mixture was cooled to 0°C and hydrolyzed with 3% HCl. The solvent and low-boiling side products were then removed under vacuum at room temperature from the separated organic layer, and the residue was placed at the top of a 40 × 2 cm glass chromatography column that was slurry packed with Florisil in hexane. The tetraorganotins were eluted with 200 mL of hexane. Elution with a mixture of hexane and ethyl acetate (4:1 by volume) recovered any triorganotin halides that may have formed. These latter products, when they occasionally occurred, could be used directly for synthesis of the copolymers. The solvents were again removed, under vacuum, from each fraction.

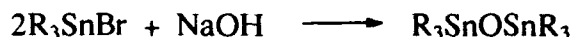
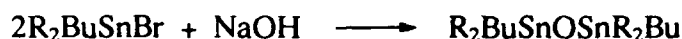
The product recovered in the hexane fraction was suspended in approximately 50 mL of methanol and cooled to 0°C in an ice bath. A stoichiometric amount of bromine in 50 mL of methanol was added dropwise in dim light to the stirred tetraorganotin suspension (Rosenberg, Debreczeni, & Weinberg, 1959; Boue, Gielen, & Nasielski, 1968; Boue et al., 1969). Upon completion of the reaction, the solvent and low-boiling side products were removed under vacuum at room temperature. The crude product was washed through a Florisil column first with hexane to recover any unreacted tetraorganotin and then with 4:1 (v/v) hexane/ethyl acetate to selectively elute the triorganotin bromide. Solvent was then removed under vacuum. Thus, six distinct products were formed: dibutyl-1-butenyltin bromide, butyldi-1-butenyltin bromide, tri-1-butenyltin bromide, dibutyl-3-butenyltin bromide, butyldi-3-butenyltin bromide, and tri-3-butenyltin bromide.

SYNTHESIS OF ORGANOTIN COPOLYMERS

The butenyltin copolymers were prepared by a modification of the procedures delineated by David Taylor Research Center, Annapolis, MD (Houghton et al., 1988).

In the original procedure, methacrylic acid and methylmethacrylate were first copolymerized, then tributyltin oxide was esterified to the methacrylic acid residue. Because of the small amounts of polymer being prepared and the unique properties of the organotin compounds being bound into the polymer, the procedure was modified so that the ester was formed before copolymerization.

The triorganotin bromides were dissolved in hexane and shaken 10 minutes in a separatory funnel with an excess of 0.1N NaOH to form the triorganotin oxide.



where R = 1-butenyl or 3-butenyl and Bu = butyl. The hexane layer was dried by filtration through anhydrous Na_2SO_4 . To prepare the methacrylic acid ester of the organotin compound, a stoichiometric amount of methacrylic acid was added and the solution was refluxed for approximately 3 hours. The solution was dried by filtration through anhydrous Na_2SO_4 , and the solvent was removed under vacuum at room temperature.



The dry, solvent-free methacrylic acid ester is then mixed with an appropriate amount of methylmethacrylate. The final proportions of monomers (total) 2-butanone and methanol should be 10:1.6:14.3, respectively. One mole percent (relative to the total monomers) of 2,2'-azobis-2-methylpropionitrile, the initiator, was dissolved in the 2-butanone. These reactants were mixed together and heated under reflux at 65°C for approximately 3 hours, by which time a thick, random copolymer formed. The solvent was left in the copolymer to facilitate painting the product onto surfaces for testing. The synthesis reaction scheme is shown in figure 1.

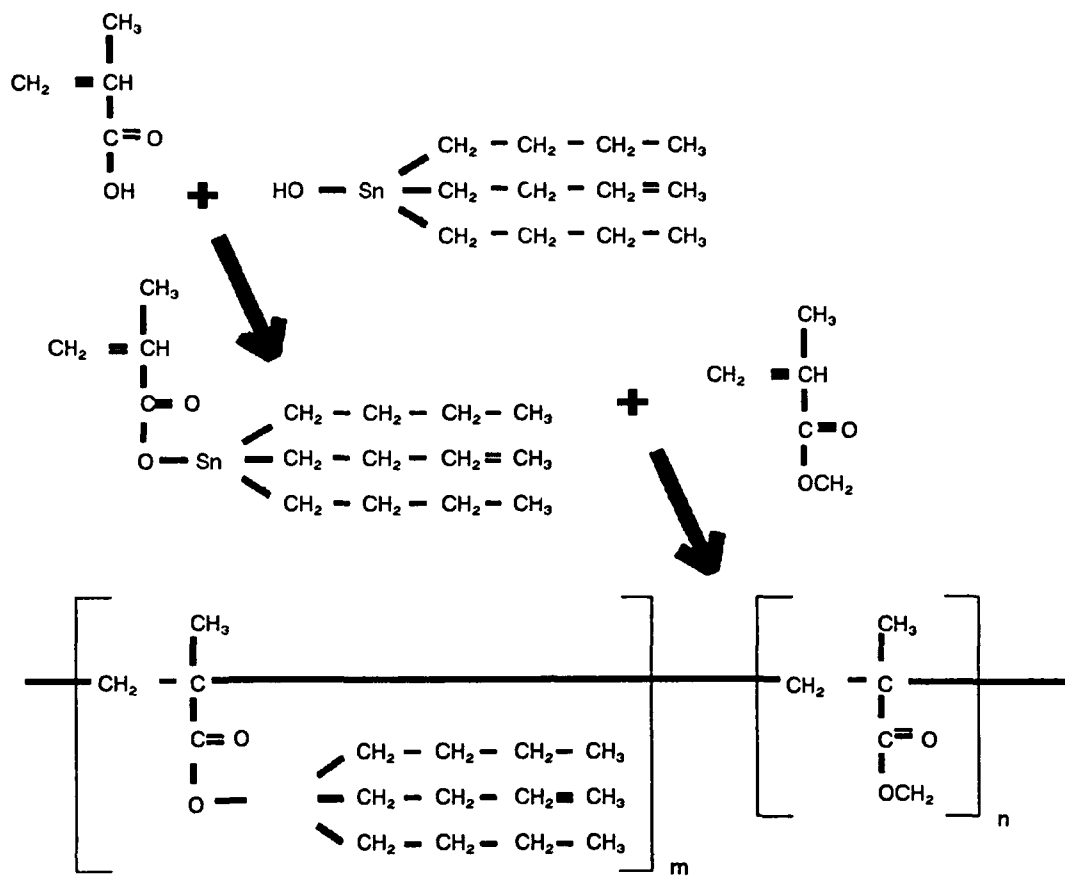


Figure 1. Synthesis of copolymers.

TOXICITY TESTING

For Microtox^R testing, stock solutions of the organotins were first prepared in 95% ethanol at approximately 1 to 2 mg/mL. Appropriate amounts of the ethanol stock solutions were then added to 2% aqueous NaCl to achieve a working standard concentration of approximately 1 ppm.

The Microtox^R Toxicity Analyzer Model 2055 (Microbics Corporation, Carlsbad, CA) is used as a bioassay that measures the relative reduction in light output by a luminescent marine bacterium, *Photobacterium phosphoreum* NRRL B-11177, when exposed to a toxicant (Bulich, 1982; Bulich & Isenberg, 1981). Serial dilutions of each compound for measurement are performed in the Microtox^R at 15°C. Light output measurements are made 5 and 15 minutes after exposure to the toxicant. The toxicity value is expressed as an EC₅₀ concentration, which is the effective concentration of a compound that caused a 50% reduction in light output. The EC₅₀ concentrations were

determined by graphic interpolation on log-log paper after plotting the ratio of the amount of light lost to the amount of light remaining against concentration.

PREPARATION AND TESTING OF THE COATED SUBSTRATES

The reaction solvent was left in the copolymer; viscosity was adjusted with additional methanol and 2-butanone. Glass and Plexiglas substrates were first painted with epoxy primer and allowed to dry overnight. The experimental organotin copolymers were coated over the epoxy and the coating system allowed to cure 1 week. The release rates were determined before exposure and after measured exposure periods. Hydride derivatization/atomic absorption spectrophotometry was used to measure concentrations as the sensitivity of the technique allowed a minimum sample volume to be removed from the seawater test reservoir. The release rate was determined in the laboratory by submersing coated substrates in stirred beakers of seawater, removing aliquots of the seawater at timed intervals, and measuring the concentration of tin-containing species hydrolyzed from the coating as a function of area of the coating and time. Selected ion mode GC/MS was used to verify the identity of the released species and the degradation products.

RESULTS AND DISCUSSION

The synthesis of tributenyltin bromides, where all three carbon chains contain double bonds at C-1, C-2, or C-3, has been previously reported (Dooley & Testa, 1989a, Dooley & Testa, 1989b; Dooley, 1990; and Dooley & Lindner, 1991). Data on identification, stability, and toxicity are also available in those references. Syntheses of the mixed saturated/unsaturated tetraorganotin compounds presented no great difficulty as long as the Grignard reagent was present in large excess to assure complete alkylation. The compounds were all stable as neat compounds and in inert solvents. Bromination of the mixed-chain tetraorganotins to produce the desired mixed-chain triorganotin bromides resulted in more side products with fewer carbon chains and more bromines than desired, than was the case with the compounds where all carbon chains were identical. I did not seek to rectify this problem, if there is a solution, and accepted the net effect of a lower than expected yield of the desired compounds.

Loss of only one chain from the triorganotin molecule to produce a diorganotin species was sufficient to reduce toxicity by an order of magnitude. The Microtox^R bioassay was a quick, inexpensive means to determine the comparative toxicity of substances. Previously, a wide range of alkyltin compounds and several alkenyltin compounds were compared in this manner (Dooley & Kenis, 1987). The ordinate axis, relative toxicity, was derived from the reciprocal EC₅₀. An arbitrary value of 100, indicating the highest toxicity, was assigned to tributyltin bromide; the other values were normalized to 100. Figure 2 shows the comparative toxicity of tributyltin (R₃Sn) and its

degradation products, dibutyltin (Bu_2Sn) and butyltin (BuSn) with the Microtox[®] system. Toxicity was reduced to an insignificant level with loss of one or more organic chains. Figure 2 also shows that the toxicities of the mixed-chain compounds were intermediate between tributyltin bromide (Bu_3Sn), which has only saturated chains, and tri-3-butenyltin bromide (R_3Sn), which has only unsaturated chains. RBu_2Sn is the compound containing one chain with the double bond at C-3; R_2BuSn is the compound with two chains containing a double bond at C-3. Data are not shown for the compounds with double bonds at C-1 because *cis/trans* isomers are possible, leading to uncertainty in the composition of the test mixture. Previous studies have shown these compounds, albeit a mixture of isomers, to be somewhat less toxic than the compounds with the double bond at C-3.

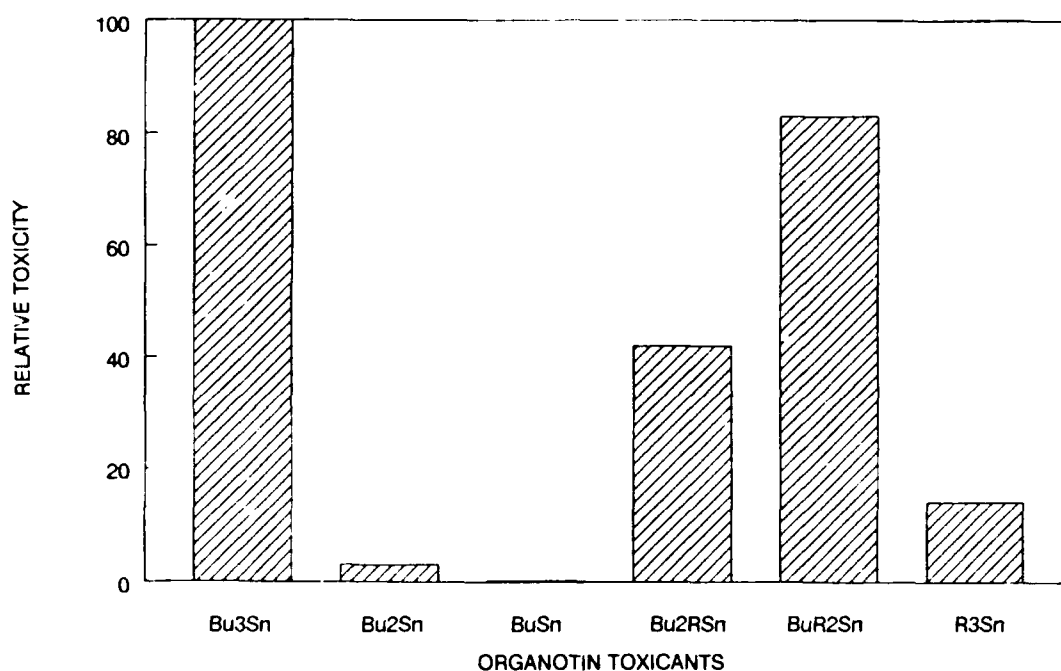


Figure 2. Comparative Microtox[®] response.

Initially, I attempted to synthesize random 50:50 copolymers for feasibility studies. A 50:50 random copolymer of methylmethacrylate and methacrylic acid was selected as the coating matrix because this polymer, chemically bonded to tributyltin, comprises the bulk of OMP-2, one of the more successful organometallic copolymer paints used as antifouling coatings. No pigments or binders were added to duplicate actual coating formulations.

Copolymers containing tributyltin were routinely polymerized before esterification. Empirically, I found that the ester of these new triorganotin species and methacrylic acid should be prepared before polymerization with methylmethacrylate to attain a usable polymer. This synthesis scheme was a significant departure from the usual route

of preparing this type of copolymer. A polymer with no toxicant and a polymer containing tributyltin were also prepared to test modifications to the suggested procedures and to function as comparison and controls for the new organometallic copolymers.

The properties of the final polymers, experimental and controls, are shown in table 1. The first column shows the toxicant that was esterified to the methacrylic acid; double bond position and the number of chains that contain the double bond are shown in the second and third columns. The solubility characteristics of the formed polymer in the preparation solvent are indicated in the fourth column. The final column shows the conditions of the formed polymer after coating and drying.

Table 1. Properties of prepared 50:50 copolymers.

Toxicant	Double Bond Position	# Unsaturated Chains	Solubility	Condition of Polymer
None	None	None	Soluble	Clear, Hard
Tributyltin	None	None	Soluble	Clear, Hard
Dibutyl-1-butenyltin	C-1	1	Dispersion	Opaque, Fragile
Butyl-di-1-butenyltin	C-1	2	Insoluble	Granular
Tri-1-butenyltin	C-1	3	Insoluble	Granular
Dibutyl-3-butenyltin	C-3	1	Soluble	Clear, Hard
Butyl-di-3-butenyltin	C-3	2	Soluble	Translucent, Hard
Tri-3-butenyltin	C-3	3	Insoluble	Granular

The physical properties of these polymers varied with the number of unsaturated chains and the position of the double bond. Copolymers containing three butenyl groups, regardless of double bond position, and the copolymer containing two 1-butenyl chains were insoluble in the preparation solvent and precipitate from solution to form a granular product. Three of the possible combinations of saturated/unsaturated chains resulted in polymers suitable as coatings: organotin compounds with double bonds at C-3 in one or two chains and organotin compounds with the double bond at C-1 in just one of the chains. The copolymers containing one or two chains with 3-butenyl groups as well as the two control polymers form smoothly spreading solutions and dry to a clear film. The copolymer containing 1-butenyl chain is a sticky lump that forms a

dispersion in the solvent and not a true solution. It dries to a white film that may yet be amenable if coated on an appropriate substrate. Laboratory tests show that this polymer adheres to an undercoat of epoxy primer. This phase of the project was described previously (Dooley, 1991).

Release rate of the toxicant through hydrolysis of the ester linkage between copolymer backbone and organotin species and the toxicity of the organotin determine the antifouling effectiveness. Besides these important laboratory studies, comparative field tests are necessary to select those coatings whose performance suggests good candidates for ship hull protection. Several types of field tests were performed: those intended to determine sustained release rates and antifouling efficacy and those to simulate ship hull performance through cycled static and dynamic testing. The various formulations undergoing exposure testing are summarized in table 2.

The first set of polymers, which consisted of all the soluble copolymers, was coated over epoxy primer on microscope slides. Different replicate slides were used for initial release rate studies and for exposure studies. The abbreviations B-00, B-11, B-31, and B-32 were used to denote copolymers containing tributyltin, dibutyl-1-butenyltin, dibutyl-3-butenyltin, and butyldi-3-butenyltin, respectively. The first digit designated the position of the double bond; the second digit defined the number of chains containing that double bond. The percentage figure (%) designated the amount of tin-bearing monomer by weight used to produce the random copolymer. COPOLY is a 50:50 random copolymer of methylmethacrylate and methacrylic acid (no toxicant) used as a control. Copolymers containing random 50:50 mixture of methylmethacrylate and methacrylic acid ester of triorganotin were first selected for testing because this formulation mimics the formulation OMP-2, as mentioned previously. No pigments or binders were added to duplicate actual coating formulations. Initially, the copolymers were coated on glass microscope slides over an epoxy primer base. Replicate slides were exposed in San Diego Bay in August 1991 to determine which coatings, if any, showed antifouling performance. Five months of exposure data were gathered on these coatings before winter storms destroyed the exposure racks. B-11 failed to prevent fouling, as did the control COPOLY; B-00, B-31, and B-32 showed good performance. Release rates were determined on a reserved set of replicates, as well as the surviving exposed microscope slides, B-00 and B-31; unfortunately, all the B-32 slides were lost.

Table 2. Exposure and testing history.

Start Date	Polymer	Release Rates ($\mu\text{g Sn/cm}^2/\text{day}$)				Comments
		Initial R3Sn	Initial R2Sn	Exposed R3Sn	Exposed R2Sn	
8/27/91	B-00 (50%)	3.33	0.68	0.13	0.05	Coated microscope slides
	B-11 (50%)	NA	NA	NA	NA	Exposure rack destroyed by February storms
	B-31 (50%)	0.16	3.8	0.068	0.36	Release rate remeasured after 6 months
	B-32 (50%)	0.3	0.73	NA	NA	Different samples used for each release measurement
	COPOLY (50%)	NA	NA	NA	NA	
5/8/92	B-00 (50%)	10.95	0.09	11.2	0.85	Exposure racks redesigned and strengthened
	B-31 (50%)	3.85	0.9	1.46	0.88	Plexiglas coupons, one set used for release rates
	B-32 (50%)	1.09	0.46	1.16	0.42	Release rate remeasured after 3 months
	COPOLY (50%)	NA	NA	NA	NA	Same sample used for release rate measurement
5/12/92	B-00 (50%)	NA	NA	NA	NA	Curved Plexiglas panels, painted in strips
	B-31 (50%)	NA	NA	NA	NA	Dynamic cycle 6/11/92 to 7/14/92; otherwise static
	B-32 (50%)	NA	NA	NA	NA	
	COPOLY (50%)	NA	NA	NA	NA	
7/15/92	B-00 (10%)	0.25	0.09	NA	NA	Plexiglas coupons, one set used for release rates
	B-00 (20%)	0.96	0.16	NA	NA	
	B-00 (35%)	5.51	0.33	NA	NA	
	B-00 (50%)	14.66	1.11	NA	NA	
	B-31 (10%)	0.06	0.03	NA	NA	
	B-31 (20%)	0.15	0.11	NA	NA	
	B-31 (35%)	0.57	0.27	NA	NA	
	B-31 (50%)	3.95	0.95	NA	NA	
	B-32 (10%)	0.04	0.02	NA	NA	
	B-32 (25%)	0.66	0.17	NA	NA	
	B-32 (50%)	2.2	0.68	NA	NA	
	COPOLY (50%)	NA	NA	NA	NA	
7/15/92	B-00 (10%)	NA	NA	NA	NA	Curved Plexiglas panels, painted in strips Dynamic cycle projected to begin 9/23/92
	B-00 (20%)	NA	NA	NA	NA	
	B-00 (35%)	NA	NA	NA	NA	
	B-00 (50%)	NA	NA	NA	NA	
	B-31 (10%)	NA	NA	NA	NA	
	B-31 (20%)	NA	NA	NA	NA	
	B-31 (35%)	NA	NA	NA	NA	
	B-31 (50%)	NA	NA	NA	NA	
	B-32 (10%)	NA	NA	NA	NA	
	B-32 (25%)	NA	NA	NA	NA	
	B-32 (50%)	NA	NA	NA	NA	
	COPOLY (50%)	NA	NA	NA	NA	

Subsequent exposures were made on Plexiglas coupons coated with the epoxy primer, which were secured to redesigned racks. Release rates were obtained after curing and before exposure, and then after a measured exposure time, the same replicate was used for all release rates. In addition, the copolymers were painted onto curved Plexiglas panels in strips to test their performance under static and dynamic conditions

meant to simulate ship use. These coatings are ablative; surfaces are continually renewed by ship movement. B-11 was dropped from the testing program because it exhibited no antifouling properties. B-00, B-31, and B-32 continue to resist fouling after 6 months; B-32 has a somewhat roughed surface character that makes it, subjectively, somewhat more difficult to remove the slight biofilm fouling before post-exposure release rates are measured. We have, as yet, no objective way of determining ease of cleaning. Release rates decline from their initial values upon exposure. This is normal behavior for all antifouling coatings.

The final set of polymers prepared and coated onto Plexiglas coupons had different weight percentages of the tin-bearing monomer. The purpose of these formulations was primarily to determine the minimum release rates that still resist fouling and to determine a composition that might improve the surface characteristics of the B-32 formulation. Changing the proportion of tin-bearing monomer changes the release rates of the coatings. The measured initial release rates for the triorganotin species are shown in figure 3. The sudden increase in release rate above 20 to 25% tin-bearing monomer parallels an abrupt increase in antifouling performance. It appears that a minimum of 25% triorganotin-containing monomer is necessary for good antifouling performance.

The most important result of the release rate studies is shown in figure 4. While B-00 primarily releases the toxic triorganotin species as expected, primarily di- and mono-organotin species are found in the seawater when B-31 and B-32 are tested for release rate. However, all formulations above 25% by weight of tin-bearing monomer show good antifouling results, regardless of the amount of triorganotin found in the test seawater. Triorganotin was recovered from the polymer surface with a gentle ethanol wash, indicating that the bound species was the triorganotin. Degradation of the mixed-chain triorganotin species to the less toxic di- and mono-organotin species appears to occur within the first 15 minutes of its hydrolysis from the polymer backbone, as this is the fastest measurement that can be made. Furthermore, GC/MS studies have shown that, as predicted, the chains containing the double bonds are preferentially cleaved from the molecules. If these results are consistent, the experimental coatings are performing even better than expected. It was initially believed that the unsaturated triorganotins would degrade more quickly than those with fully saturated chains once released by hydrolysis from the polymer backbone. It now appears that hydrolysis is nearly simultaneous with degradation by loss of an organic sidechain. When not incorporated into a polymer backbone, the toxicant compound did not degrade quickly in seawater, regardless of whether it was added as a halide or an ester.

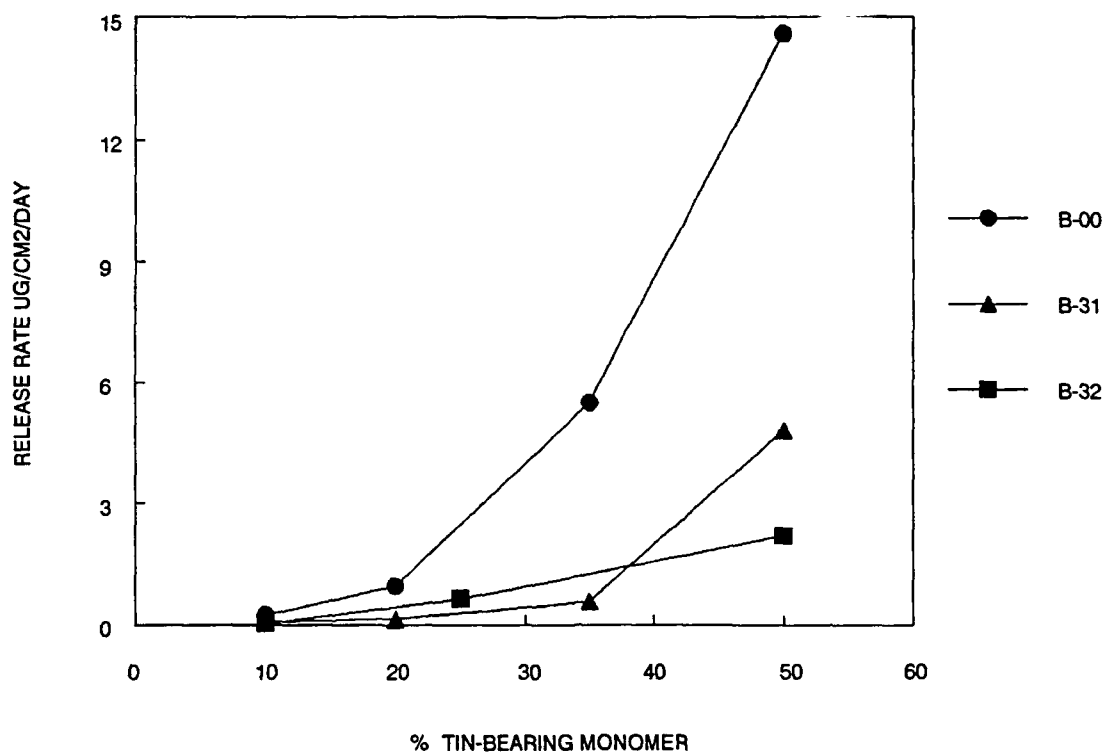


Figure 3. Initial release rates of triorganotin.

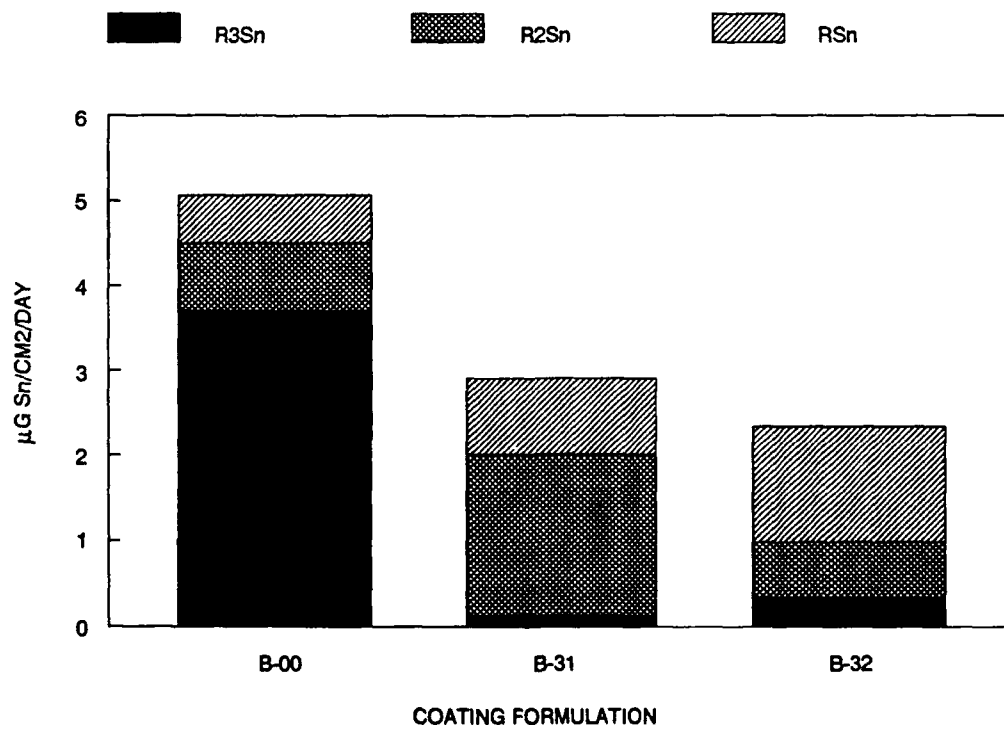


Figure 4. Release rates of tin species.

CONCLUSIONS

Triorganotin toxicants composed of mixed saturated and unsaturated four-carbon chains with double bonds at C-1 and C-3 were prepared. Incorporation of these compounds into random 50:50 copolymers of methacrylic acid and methylmethacrylate resulted in three copolymer compositions with promising physical properties for use as antifouling coatings for ship hulls. These formulations were screened for stability and antifouling in San Diego Bay.

Copolymers of methylmethacrylate and methacrylic acid esterified with dibutyl-3-butenyltin (B-31) and butyldi-3-butenyltin (B-32) show antifouling performance equivalent to copolymer containing tributyltin (B-00) after 6 months in the field. Release rate studies show that a minimum of 25% tin-bearing monomer is necessary for good antifouling properties for all formulations. Degradation of the toxicant species with double bonds, through loss of organic chains, appears to be near simultaneous with its release, through hydrolysis of the ester bond, from the coating. Thus, after prevention of fouling by surface toxicity to target organisms, the released species has a minimal impact on the environment.

REFERENCES

- Boue, S., M. Gielen, and J. Nasielski. 1968. "Organometallic Compounds. VII. Electron Impact Fragmentation of Some Mixed and Symmetrical Tetraalkyltins," *Bulletin Societe de Chimie Belge*, vol. 77, p. 43.
- Boue, S., M. Gielen, J. Nasielski, J. P. Lieutenant, and R. Spielmann. 1969. "Organometallic Compounds. XI. Synthesis and Properties of a Series of Racemic Tetraalkyltins," *Bulletin Societe de Chimie Belge*, vol. 78, p. 135.
- Bulich, A. A. 1982. "A Practical and Reliable Method for Monitoring the Toxicity of Aquatic Samples," *Process Biochemistry*, March/April, p. 45.
- Bulich, A. A., and D. L. Isenberg. 1981. "Use of the Luminescent Bacterial System for the Rapid Assessment of Aquatic Toxicity," *ISA Transactions*, vol. 20, no.1, p. 29.
- Clark, H. C., and R. C. Poller. 1970. "Pi-bonding between C=C Bonds and Tin in Alkenyltin Compounds," *Canadian Journal of Chemistry*, vol. 48, p. 2670.
- Cochran, J. C., S. C. Bayer, J. T. Bilbo, M. S. Brown, L. B. Colen, F. Gaspirini, D. W. Goldsmith, M. D. Jamin, K. A. Nealy, C. T. Resnick, G. J. Schwartz, W. M. Short, K. R. Skarda, J. P. Spring, and W. L. Strauss. 1982. "Kinetics of the Protodestannylation of Vinyltrialkyltins and Substituted Vinyltrialkyltins," *Organometallics*, vol. 1, p. 586.
- Davies, A. G., and P. J. Smith. 1982. *Comprehensive Organometallic Chemistry*; Wilkinson, G., F. G. A. Stone, and E. W. Abel (Ed); Pergamon Press, New York, pp. 519-627.
- Dooley, C. A. 1990. "Synthesis, Stability and Toxicity of Organotin Antifoulant Compounds with Unsaturated Carbon Chains." In IR-IED '90, NOSC TR 1957, vol. 2, p. 13. Naval Ocean Systems Center, San Diego, CA.
- Dooley, C. A. 1991. "Antifouling Copolymers for Ship Hull Protection: Unsaturated Organotin Compounds," NOSC TN 1664*. Naval Ocean Systems Center, San Diego, CA.
- Dooley, C. A., and P. Kenis. 1987. "Response of Bioluminescent Bacteria to Alkyltin Compounds," *Oceans 87*, vol. 4, p. 1517.
- Dooley, C. A., and E. Lindner. 1991. Organotin Compounds, U. S. Patent No. 5,006,554, 9 April 1991.
- Dooley, C. A., and J. P. Testa, Jr. 1989a. "Synthesis and Mass Spectra of Butenyltin Compounds," NOSC TR 1272. Naval Ocean Systems Center, San Diego, CA.
- Dooley, C. A., and J. P. Testa, Jr. 1989b. "Stability and Microtox Response of Butenyltin Compounds," *Applied Organometallic Chemistry*, vol. 3, p. 171.

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- Houghton, D. A., T. Juska, T. Dapp, W. B. Mercer, and V. Castelli. 1988. "Synthesis and Characterization of Controlled Release Organotin Containing Polymers," DTRC/SME-87/94.
- Ingham, R. K., S. D. Rosenberg, and H. Gilman. 1960. "Organotin Compounds," *Chemical Reviews*, vol. 60, p. 459.
- O'Brien, S., M. Fishwick, B. McDermott, M. G. H. Wallbridge, and G. A. Wright. 1971. "Isoleptic Allyl Derivatives of Various Metals," *Inorganic Synthesis*, vol. 13, p. 73.
- Rosenberg, S. D., E. Debreczeni, and E. L. Weinberg. 1959. "The Preparation of Some Unsymmetrical Organotin Bromides and Acetates," *Journal of the American Chemical Society*, vol. 81, p. 972.
- Rosenberg, S. D., A. J. Gibbons, Jr., and H. E. Ramsden. 1957. "The Disproportionation of Tetravinyltin with Tin Tetrachloride and the Cleavage of Some Vinyltin Compounds with Bromide," *Journal of the American Chemical Society*, vol. 79, p. 2137.
- Seyferth, D., and F. G. A. Stone. 1957. "Vinyl Derivatives of the Metals. I. Synthesis of Vinyltin compounds," *Journal of the American Chemical Society*, vol. 79, p. 515.
- Stallard, M. O., S. Y. Cola, and C. A. Dooley. 1989. "Optimization of Butyltin Measurements for Seawater, Tissue, and Marine Sediment Samples," *Applied Organometallic Chemistry*, vol. 3, p. 105.
- Valkirs, A. O., P. F. Seligman, G. Vafa, P. M. Stang, V. Homer, and S. H. Lieberman. 1985. "Speciation of Butyltins in Seawater and Marine Sediments by Hydride Derivatization and Atomic Absorption Detection," NOSC TR 1037. Naval Ocean Systems Center, San Diego, CA.
- Vijayaraghavan, K. V. 1945. "Organometallic Compounds of the Allyl Radical. Part II. Tin Tetra Allyl and its Derivatives," *Journal of the Indian Chemical Society*, vol. 22, p. 135.

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